RESEARCH LETTER

10.1002/2017GL074962

Key Points:

- Under stationary conditions, aquifer residence time distributions can be estimated from outflow age distributions, and vice versa
- For a given mean flow age, river waters that are skewed toward younger ages imply aquifer waters that are older on average
- Tracer data imply that streamflow mostly comes from a thin veneer of groundwater, and most storage must be relatively old by comparison

Correspondence to:

W. R. Berghuijs,
wouter.berghuijs@usys.ethz.ch

Citation:

Berghuijs, W. R., and J. W. Kirchner (2017), The relationship between contrasting ages of groundwater and streamflow, *Geophys. Res. Lett.*, *44*, 8925–8935, doi:10.1002/2017GL074962.

Received 15 JUL 2017

Accepted 24 AUG 2017

Accepted article online 29 AUG 2017

Published online 9 SEP 2017

The relationship between contrasting ages of groundwater and streamflow

Wouter R. Berghuijs¹ and James W. Kirchner^{1,2,3}
¹Department of Environmental Systems Science, ETH Zurich, Zürich, Switzerland, ²Swiss Federal Research Institute WSL, Birmensdorf, Switzerland, ³Department of Earth and Planetary Science, University of California, Berkeley, California, USA

Abstract Tracer data demonstrate that waters in aquifers are often much older than the stream waters that drain them. This contrast in water ages has lacked a general quantitative explanation. Here we show that under stationary conditions, the age distribution of water stored in a catchment can be directly estimated from the age distribution of its outflows, and vice versa. This in turn implies that the storage selection function, expressing the catchment's preference for the release or retention of waters of different ages, can be estimated directly from the age distribution of outflow under stationary conditions. Using gamma distributions of streamflow ages, we show that the mean age of stored water can range from half as old as the mean age of streamflow (for plug flow conditions) to almost infinitely older (for strongly preferential flow). Many streamflow age distributions have long upper tails, consistent with preferential flow and implying that storage ages are substantially older than streamflow ages. Mean streamflow ages reported in the literature imply that most streamflow originates from a thin veneer of total groundwater storage. This preferential release of young streamflow implies that most groundwater is exchanged only slowly with the surface and consequently is relatively old.

1. Introduction

Many streams respond promptly to rainstorms, even though storm runoff often contains relatively little water that originates from current rainfall [Sklash and Farvolden, 1979; Kirchner, 2003; McDonnell and Beven, 2014]. Typical aquifers feeding these streams consist mostly of water that is decades to millennia in age [Gleeson et al., 2016; Jasechko et al., 2017]. In contrast, significant fractions of typical river flows are less than approximately 3 months old [Jasechko et al., 2016], indicating that river waters are generally much younger than the aquifers that feed them. Two distinct water age concepts must be distinguished here: (i) the residence time (the age, since its time of entry, of water stored in a catchment) and (ii) the transit time (the age, since its time of entry, of water leaving the catchment) [Bolin and Rodhe, 1973; Rinaldo et al., 2011]. Understanding a catchment's residence times and transit times is essential for quantifying hydrological processes [Kirchner, 2003; McDonnell and Beven, 2014; Hrachowitz et al., 2016] and for understanding biogeochemical cycles, contaminant transport, and chemical weathering [Gibbs, 1970; Kirchner et al., 2000; Stark and Stieglitz, 2000; Austin et al., 2004; Basu et al., 2010]. However, a simple, general explanation for the age dichotomy between rivers and their aquifers has remained elusive.

The age contrast between rivers and aquifers seems paradoxical: catchments' aquifers feed their rivers, so how can they be so much older than the rivers that drain them? However, simple physically based reasoning suggests that these age contrasts should be expected wherever aquifers are heterogeneous (which is to say: everywhere). As a simple example, consider a hypothetical aquifer (Figure 1) characterized by porosity (ϕ), a head gradient (ΔH) that drives darcy flow (q) over a length (L) and two equally thick transmitting layers with contrasting conductivities ($K_1 \neq K_2$). The flow velocities (v) and the volumetric fluxes in each layer will be proportional to their conductivities ($v_i = K_i(\Delta H/L)/\phi$); in contrast, the ages of the waters flowing out of each layer (τ_i) will be inversely proportional to their velocities and thus their conductivities ($\tau_i = L/v_i = (L^2 \cdot \phi)/(\Delta H \cdot K_i)$). Note that relative to its low-conductivity counterpart, the high-conductivity flow path will transmit more water (because it flows faster) and its discharge will be younger (because, again, it flows faster). Thus, the greater the contrast in conductivity, the older the volume-weighted mean age of water in the aquifer will be ($\tau_r = (\phi/4)(L^2/\Delta H) \cdot (1/K_1 + 1/K_2)$) in comparison to the flow-weighted mean age of water exiting the aquifer ($\bar{\tau} = 2\phi(L^2/\Delta H)/(K_1 + K_2)$); the ratio between these means will be $\tau_r/\bar{\tau} = 0.25 + (K_1/K_2 + K_2/K_1)/8$. Similar discordance between aquifer discharge and storage ages is also seen in more complex aquifer models [e.g.,

Figure 1. Flow-weighted mean transit time (mean water age at exit) and volume-weighted mean residence time (mean water age of resident water) for a simple two-component aquifer with contrasting conductivities ($K_1 \neq K_2$). The mean age of water in the aquifer (τ_r) is much older than the mean age of discharged water ($\bar{\tau}$) whenever there is a strong conductivity contrast, such that $K_1 \gg K_2$ or $K_1 \ll K_2$; the ratio between the mean ages is $\tau_r/\bar{\tau} = 0.25 + (K_1/K_2 + K_2/K_1)/8$.

Cardenas, 2007, 2008; Wörman *et al.*, 2007]. Given that aquifer conductivities can vary by orders of magnitude [Gleeson *et al.*, 2011], even within an individual catchment [Ameli *et al.*, 2016], it is not surprising that the mean ages of groundwaters and river waters can strongly differ. Other runoff generating mechanisms, such as overland flow [Horton, 1933; Dunne, 1978] and preferential flow [Beven and Germann, 1982, 2013], can lead to similar contrasts in fluxes and flow velocities along different flow paths, resulting in age contrasts between streamflows and aquifers similar to those described here.

In addition to this hypothetical example, ages of flow and storage can also be quantified using simple physically based models for several other idealized aquifer representations [e.g., Chesnaux *et al.*, 2005; Leray *et al.*, 2016]. However, none of these approaches can quantify the effects of the more complex (and poorly characterized) flow path heterogeneity that is typically encountered in real-world catchments [McDonnell *et al.*, 2007]. Spatially explicit models can represent more of the heterogeneity that is present at the catchment scale [e.g., Kollet and Maxwell, 2008; Engdahl and Maxwell, 2015; Maxwell *et al.*, 2016]. However, representing the spatial complexity that characterizes real-world landscapes, especially in the subsurface, requires model assumptions and parameterizations that cannot be validated [Berkowitz, 2002; Beven, 2006]. In addition, such model simulations can at best reproduce the observed water age distributions only for particular cases, rather than quantitatively explaining the general contrast between catchment-scale residence times (of storage) and transit times (of streamflow).

Theoretical relationships between transit times and residence times of natural reservoirs (e.g., the atmosphere and ocean) were established decades ago using reservoir theory [Eriksson, 1961, 1971; Bolin and Rodhe, 1973]. Reservoir theory describes the conservation of mass and age in reservoirs and their outgoing fluxes. Under steady-state conditions, it can be used to infer the functional relationship between transit times and residence times. This relationship is in essence a specific case of the more general *storage selection function* framework [Botter *et al.*, 2011; van der Velde *et al.*, 2012; Harman, 2015; Rinaldo *et al.*, 2015], which can be used to parameterize time-varying preferences for catchments to release water parcels of different ages. So far, applications of storage selection functions have mainly focused on relationships between time-varying age distributions of streamflow and storage [e.g., Botter, 2012; Harman, 2015; Kim *et al.*, 2016; Benettin *et al.*, 2017], rather than exploring the steady-state case, which we explore here and which yields a unique relationship between transit times and residence times. Reservoir theory has previously been used to investigate particle-age fluxes through bounded domains (e.g., aquifers) [Etcheverry and Perrochet, 2000; Cornaton and Perrochet, 2006a, 2006b; Kazemi *et al.*, 2006], but an application for catchment-scale hydrology that clarifies and quantifies the connection between contrasting ages of streamflow and storage has not previously been attempted.

Here we apply reservoir theory to catchment-scale water partitioning and use it to show the quantitative linkage between transit time distributions and residence time distributions under stationary conditions (section 2). We provide examples of the relative age distributions of storage and streamflow, using gamma distributions as simple models for streamflow transit times (section 3). To illustrate the potential

Figure 2. The basic definitions of catchment storage and outflow and conservation of mass and age, illustrated by (hypothetical) steady-state age distributions. In steady state, the rate that stored water reaches a given age (the probability density function of stored water age times total storage, shown in the leftmost plot) must equal the outflow rate of all water of that age or older (the complementary cumulative distribution of outflow age times the mean outflow rate, the inverse of the rightmost plot).

of this approach, we use it to infer storage ages based on a range of streamflow age distributions reported in the literature (section 4).

2. Connection Between Storage and Outflow

Here we review basic principles of reservoir theory [Eriksson, 1961, 1971; Bolin and Rodhe, 1973] and outline its application to catchment-scale hydrology. We define the total water storage in a catchment as S_0 ; its corresponding cumulative age distribution $S(\tau)$ is the fraction of water in storage that has an age (since it has entered the catchment) of less or equal to τ . From $S(\tau)$, we can define the probability density function $\psi(\tau)$ of storage with respect to age τ (i.e., $\psi(\tau) = dS/d\tau$). Outflow has a constant rate $\bar{O}$ and a cumulative age distribution $O(\tau)$ that expresses the fraction of water leaving the catchment that has an age (since entry) of less than or equal to τ . From $O(\tau)$, we define the probability density function $\phi(\tau)$ of outflow with respect to age (i.e., $\phi(\tau) = dO(\tau)/d\tau$) (Figure 2). Note that outflow encompasses all water fluxes leaving the catchment, including evapotranspiration.

The age distributions of storage and outflow can be linked based on the conservation of mass and age. In steady state, the amount of water that reaches age τ per unit of time (i.e., $S_0 \psi(\tau)$) must equal the flux leaving the catchment per unit time with an age older than τ (i.e., $\bar{O}(1 - O(\tau))$), leading directly to

$$\bar{O}(1 - O(\tau)) = S_0 \psi(\tau). \quad (1)$$

Simply stated: in steady state, the *complementary cumulative* age distribution of outflow, times the mean flow rate, must equal the *probability density* function of water ages in storage, times the total storage. This is physically equivalent to the steady-state solutions of mass and age conservation of equations described in earlier work [e.g., Ginn, 1999; Botter et al., 2011; van der Velde et al., 2012; Harman, 2015]. The conservation of mass and age that we describe here can be applied to any reservoir that is in steady state with its outgoing fluxes. (Numerical experiments with Kirchner's [2016] nonstationary two-box model show that this result also holds,

to a good approximation, in nonsteady-state systems forced by nonstationary precipitation inputs, as long as both sides of equation (1) are averaged over sufficiently long intervals. These numerical experiments are beyond the scope of the present paper and will be presented in future work.)

Conservation of mass and age (equation (1)) can be used to express the probability density functions and cumulative distributions of storage and outflow age as functions of each other. From the derivative of equation (1), one can show that the probability density function $\varphi(\tau)$ of outflow age is proportional to the derivative of the probability density function $\psi(\tau)$ of storage age:

$$\varphi(\tau) = -\frac{\bar{O}}{S_0} \frac{d\psi(\tau)}{d\tau}. \quad (2)$$

Likewise, by rearranging equation (1), one can express the probability density function $\psi(\tau)$ of storage age and the cumulative distribution $O(\tau)$ of outflow age, as functions of one another:

$$\psi(\tau) = \frac{\bar{O}(1 - O(\tau))}{S_0} \quad (3)$$

and

$$O(\tau) = 1 - \frac{S_0}{\bar{O}} \psi(\tau), \quad (4)$$

and by integrating equation (3), one can show that the storage age distribution $S(\tau)$ is the appropriately scaled integral of the outflow age distribution $O(\tau)$:

$$S(\tau) = \int_0^\tau \left(\frac{\bar{O}(1 - O(\tau))}{S_0} \right) d\tau. \quad (5)$$

The *mean transit time* of water leaving the catchment is

$$\bar{\tau} = \int_0^\infty \tau \varphi(\tau) d\tau = \frac{S_0}{\bar{O}}, \quad (6)$$

which will generally differ from the average age of particles stored (i.e., the *mean residence time*), given by

$$\tau_r = \int_0^\infty \tau \psi(\tau) d\tau. \quad (7)$$

Equations (2)–(5) describe explicit quantitative relationships between storage residence time distributions and catchment transit time distributions and thereby correspond to the stationary case of the more general (nonstationary) storage selection function framework [Botter *et al.*, 2011; van der Velde *et al.*, 2012; Harman, 2015; Rinaldo *et al.*, 2015]. Storage selection functions express catchments' tendencies to release or retain waters of different ages. Using equation (3), one can directly calculate the storage selection function under stationary conditions from the age distribution of outflow alone, without any direct information concerning the age distribution of storage:

$$\omega_O = \frac{\varphi(\tau)}{\psi(\tau)} = \frac{\varphi(\tau)}{\bar{\tau}(1 - O(\tau))}. \quad (8)$$

Conversely, one could also calculate the storage selection function under stationary conditions from the age distribution of storage alone, without any direct information concerning the age distribution of outflow:

$$\omega_O = \frac{\varphi(\tau)}{\psi(\tau)} = -\frac{d\psi(\tau)/d\tau \bar{O}}{\psi(\tau) S_0}. \quad (9)$$

Figure 3. Gamma-distributed (a) probability density functions ($p(\tau)$) and (b) cumulative distributions ($O(\tau)$) of streamflow transit times for (h) diverse shape factors (α) and catchment behaviors, and the (c) corresponding steady-state probability density functions ($\psi(\tau)$) and (d) cumulative distributions ($S(\tau)$) of aquifer storage ages, as well as the (e) corresponding steady-state storage selection functions, the relationships between the (f) cumulative storage and discharge distributions, and (g) the ratios of their means. Note that for each shape factor, the probability density function of storage ($\psi(\tau)$, Figure 3c) is the inverse of the cumulative distribution function of streamflow ($O(\tau)$, Figure 3b), as described by equation (1). For a completely mixed system (exponential distribution, $\alpha = 1$), the streamflow and storage age distributions are identical (panel f), and the associated storage selection function is $\omega_O = 1$ (Figure 3e). For preferential flow systems ($\alpha < 1$), young storage is more likely to be converted to streamflow (Figure 3e), and each quantile of the storage age distribution is older than the same quantile of the streamflow age distribution (Figure 3f), whereas the opposite is true for systems with humped streamflow age distributions ($\alpha > 1$). The mean age of stored water ranges from half as old as streamflow, for a homogenous plug flow system with $\alpha \rightarrow \infty$, to much older than the mean age of streamflow, for a heterogeneous system where most flow is preferential, with $\alpha \rightarrow 0$ (Figure 3g). The mean ages of storage and streamflow are only equal for well-mixed systems ($\alpha = 1$).

3. Age Distributions of Storage and Streamflow

To illustrate the relationship between storage and streamflow ages, here we give examples showing how specific transit time distributions of streamflow translate into storage age (Figure 3). This analysis assumes that either (a) evaporative fluxes are negligibly small, (b) they are nonnegligible but their age distribution is similar to that of streamflow, or (c) the storage in question is the storage from which streamflow is derived, rather than total catchment storage.

Gamma distributions have often been used to represent catchment transit times [e.g., Turner and Barnes, 1998; Kirchner et al., 2000; Dunn et al., 2010; Hrachowitz et al., 2010; Godsey et al., 2010; Tetzlaff et al., 2011; Heidbüchel et al., 2012; Seeger and Weiler, 2014]:

$$p(\tau) = \frac{\tau^{\alpha-1}}{\beta^\alpha \Gamma(\alpha)} e^{-\tau/\beta} = \frac{\tau^{\alpha-1}}{(\bar{\tau}/\alpha)^\alpha \Gamma(\alpha)} e^{-\alpha\tau/\bar{\tau}}, \quad (10)$$

where Γ is the gamma function, α and β are a shape factor and scale factor, respectively, τ is the transit time, and $\bar{\tau} (= \alpha\beta)$ is the mean transit time. The cumulative outflow age distribution $O(\tau)$ is as follows:

$$O(\tau) = \frac{\gamma(\alpha, \tau/\bar{\tau})}{\Gamma(\alpha)}, \quad (11)$$

where γ is the lower incomplete gamma function. Catchments have often been assumed to approximate completely mixed systems with exponential transit time distributions; this behavior can also be described by the gamma distribution, which becomes the exponential distribution in the special case that $\alpha = 1$. Dispersive transport over fixed path lengths will yield humped transit time distributions, which are approximated by the gamma distribution for $\alpha > 1$. A fixed flow path without dispersion will exhibit plug flow and will be characterized by a Dirac delta transit time distribution. This can also be approximated by the gamma distribution, which becomes arbitrarily close to the Dirac delta function as $\alpha \rightarrow \infty$.

Field data also support the use of gamma distributions as empirical models for catchment transit time distributions. Power spectra of tracer time series from many diverse catchments are broadly consistent with gamma transit time distributions with $\alpha \approx 0.5$, which have a sharp peak at short lag times and relatively long upper tails [Kirchner *et al.*, 2000, 2001; Godsey *et al.*, 2010], a result that is also supported by time domain convolutions and modeling studies [e.g., Dunn *et al.*, 2010; Hrachowitz *et al.*, 2010; Tetzlaff *et al.*, 2011; Heimbüchel *et al.*, 2012; Seeger and Weiler, 2014; Benettin *et al.*, 2017]. Real-world streamflow age distributions may not be perfectly described by a gamma distribution, and other (nonparametric) age distributions may be more realistic in specific cases. Nevertheless, gamma distributions can capture a wide range of behaviors and thus are useful for illustrating the general relationship between streamflow ages and storage ages.

Assuming hypothetical gamma distributions for outflow age, we can now directly formulate the corresponding probability density function for storage age:

$$\psi(\tau) = \frac{1}{\bar{\tau}} \left(1 - \frac{\gamma(\alpha, \tau, \bar{\tau}/\alpha)}{\Gamma(\alpha)} \right). \quad (12)$$

This means that the cumulative age distribution of storage can also be expressed as a function of α and $\bar{\tau}$:

$$S(\tau) = \frac{1}{\bar{\tau}} \int_0^\tau \left(1 - \frac{\gamma(\alpha, \tau, \bar{\tau}/\alpha)}{\Gamma(\alpha)} \right) d\tau. \quad (13)$$

$S(\tau)$ can be estimated straightforwardly by numerical integration. Based on equations (10)–(13), we calculated storage age distributions for different values of the shape factor (Figure 3). These shape factors describe very different streamflow transit time distributions and imply markedly different residence time distributions of storage, as further illustrated by the storage selection functions and the comparison of the cumulative distributions $S(\tau)$ and $O(\tau)$ in Figure 3.

The mean age of stored water (Figure 3g) ranges from half as old as streamflow (for pure plug flow, with $\alpha \rightarrow \infty$), to almost infinitely older than streamflow (for highly heterogeneous aquifers, with strongly preferential flow and $\alpha \rightarrow 0$). Only for perfectly mixed systems are the age distributions (and thus the mean ages) in storage and streamflow equal. More generally, we can say that for the same mean age of streamflow, the larger the fraction of young water in a river (the smaller the shape factor α), the older the mean age of the water in the aquifer that feeds the river. Shape factors of $\alpha \sim 0.5$, which have been reported in many catchments around the world, imply that we should generally expect aquifers to be older than the stream waters that drain them.

4. Estimating the Age of Groundwater

In real-world aquifers, groundwater ages can be inferred from isotopic and geochemical tracers in well or spring waters [e.g., Bethke and Johnson, 2008; Torgersen *et al.*, 2013; Jasechko *et al.*, 2017] but not across larger spatial domains (e.g., throughout an entire catchment). The relationship between groundwater ages and streamflow ages, derived above, potentially provides a way to constrain groundwater age distributions from estimates of stream water age distributions. Here we use the analysis presented above, along with streamflow age distributions from the literature, to provide insight into what groundwater age distributions can be expected.

There are several methods for estimating transit time distributions of streamflow [see McGuire and McDonnell, 2006], including *time domain convolution approaches* [e.g., Stewart and McDonnell, 1991; Weiler *et al.*, 2003; Hrachowitz *et al.*, 2010], *model-based approaches* [e.g., Botter *et al.*, 2011; van der Velde *et al.*, 2012; Harman, 2015], and *spectral analysis* [e.g., Kirchner *et al.*, 2000, 2001; Godsey *et al.*, 2010]. To illustrate the range of distributions that may occur in nature, we used equation (11) to obtain the cumulative age distributions of streamflow for the 5th, 25th, 50th, 75th, and 95th percentiles of α values among the 53 catchments reported in Godsey *et al.* [2010], Hrachowitz *et al.* [2010], and Seeger [2013] and used equation (13) to calculate the corresponding cumulative age distributions of storage in steady state (Figure 4). Across this range of α values,

Figure 4. (a) Cumulative streamflow gamma transit time distributions $O(\tau)$ for the 5th, 25th, 50th, 75th, and 95th percentiles of α values reported in previous studies (see text), indicated by dashed lines, and the corresponding age distributions of water storage $S(\tau)$, indicated by solid lines. (b) Total storage S_0 as a function of mean transit times $\bar{\tau}$ and mean streamflow rates $\bar{O}$, with interquartile ranges of $\bar{\tau}$ and $\bar{O}$ based on previous studies (see text) indicated by dashed lines. For the interquartile ranges of α , $\bar{\tau}$, and $\bar{O}$, ages of storage exceed streamflow ages, mean residence times range from just over a year to ~5 years, and total storage is ~0.2 to 1.2 m of equivalent water depth. The associated storage selection functions ω_O , shown on a (c) logarithmic scale and on a (d) linear scale for water age, indicate a strong preference for releasing younger waters to streamflow.

storage is significantly older than streamflow (note the logarithmic scale in Figure 4a). To illustrate how catchments release water parcels of different ages under these conditions, we also plot the associated storage selection functions ω_O . These show similar general shapes, indicating a strong preference for releasing younger waters as streamflow (Figures 4c and 4d).

The age distributions shown in Figure 4 can be converted to years, given an estimate of the mean transit time $\bar{\tau}$. Mean transit times reported in a synthesis of nearly 100 catchments [McGuire and McDonnell, 2006] yield an interquartile range of 1 to 2.4 years. This interquartile range, combined with the interquartile range of the age distributions presented in Figure 4a, yields estimates for the mean residence time of storage that range from just over a year (for $\alpha = 0.60$ and $\bar{\tau} = 1$ year) to approximately 5 years (for $\alpha = 0.38$ and $\bar{\tau} = 2.4$ years). The corresponding total volume of storage S_0 can be calculated by multiplying the mean streamflow rate and the mean transit time (equation (6): $S_0 = \bar{\tau} \bar{O}$). Global streamflow rates average $\sim 280 \text{ mm yr}^{-1}$ but vary strongly between regions [Dai and Trenberth, 2002]. For several hundred diverse catchments located across the United States [Berghuijs et al., 2014], the interquartile range of mean streamflows is 211 to 511 mm yr^{-1} . For the interquartile ranges of $\bar{\tau}$ and $\bar{O}$ shown in Figure 4b, catchment water storage S_0 ranges from 211 mm (for $\bar{\tau} = 1$ year and $\bar{O} = 211 \text{ mm yr}^{-1}$) to just over 1.2 m (for $\bar{\tau} = 2.4$ years and $\bar{O} = 511 \text{ mm yr}^{-1}$).

These storage volumes are a small fraction of global groundwater storage, which has been estimated to average 15 m in the upper 100 m of the Earth's crust and 180 m in the upper 2 km [Gleeson et al., 2016]. Our analysis therefore implies that streamflow largely comes from a thin veneer of total groundwater storage and thus that deeper groundwaters (that are not part of our estimated age distributions) must exchange only slowly with the surface. Consequently, most storage must be much older than the relatively small fraction of groundwater that most actively participates in the hydrologic cycle (which in turn will be older than streamflow). This inference is consistent with place-based groundwater-surface water modeling [Toews et al., 2016; Ala-aho et al., 2017] and more generalized topography-driven modeling of groundwater flow [Cardenas, 2007, 2008; Wörman et al., 2007]. In addition, it is consistent with recent analyses of isotope

data showing that most groundwater at depths below ~40 m is over 60 years old, and most groundwater below ~200 m depth is pre-Holocene in age [Jasechko *et al.*, 2017]. The great age of these deep, old groundwaters directly implies that they must exchange only slowly with the surface, because otherwise they could not be so old. Because they contribute a negligible fraction to streamflow, the tracer signals that they impart may be unmeasurable in streams. Because we cannot accurately constrain the extreme upper tail of the stream water age curve, the approach outlined in sections 2 and 3 above cannot be used to estimate the contribution of very old water to the storage age distribution.

Our analysis quantifies the steady-state relationship between the age distribution of storage and the age distribution of its total outflow. In catchments, this outgoing flux includes not only streamflow but also evapotranspiration, which often exceeds stream discharge [Rodell *et al.*, 2015]. Age distributions of evaporative losses have not yet been systematically measured at the catchment scale [Soulsby *et al.*, 2016]. However, we expect evapotranspiration, like streamflow, to preferentially draw from younger storage ages. A significant component of total evapotranspiration is canopy interception, which consists entirely of recent rainfall [Crockford and Richardson, 2000]. In addition, transpiration originates mostly from shallow soil water [e.g., Goldsmith *et al.*, 2012; Good *et al.*, 2015], which will generally be younger than deeper groundwaters. This means that evaporative losses are likely to have a similar (or even more skewed) age distribution compared to runoff. Consequently, we expect that if the age distribution of evaporative fluxes could be taken into account, the age contrast between storage and outflow would be at least as large as we have estimated above. Empirically determining the age distribution of evaporative fluxes will be relevant to almost any application using tracer data to understand water transport in the hydrological cycle and thus should be a focus of future research [Soulsby *et al.*, 2016]. Nonetheless, to the extent that evapotranspiration and streamflow come from different storages, the age distribution of streamflow can be used to infer the age distribution of the storage it comes from, even if the age distribution of evapotranspiration is unknown.

The age distributions of short-term (e.g., daily) streamflows are time varying [e.g., Harman, 2015; Benettin *et al.*, 2017] and thus can diverge from the steady-state solution. In contrast, groundwater storage volumes generally far exceed the volume of outflow (at event time scales), and consequently, storage age distributions tend to be much more stable. This means that even if steady-state assumptions are of limited use to predict time-varying streamflow age distribution at short time scales, they can nonetheless be useful in constraining storage age distributions and their relationships to streamflow ages averaged over longer time periods. Better estimating the accuracy of the steady-state solution for such purposes requires additional numerical experiments that are beyond the scope of the present paper and will be presented in future work.

5. Summary and Implications

Aquifers are often much older than the stream waters that drain them. This contrast in water ages can be explained as a consequence of subsurface heterogeneity, using either simple physically based reasoning (Figure 1) or more detailed modeling approaches. Under stationary conditions, conservation of mass and age implies that the amount of storage at any age τ (and thus the rate at which storage becomes older than that) must equal the cumulative outflow that exceeds the same age τ as it leaves the catchment (Figure 2 and equation (1)). For stationary catchments, simple relationships directly express the residence time distribution of storage as a function of the transit time distribution of outflow, and vice versa (equations (2)–(5)). This establishes a framework for estimating storage age distributions (which are generally unknown) from streamflow age distributions (for which tracer-based estimates may be available), if quasi-stationarity can be assumed.

The relationships explored here represent a special (stationary) case of the more general (nonstationary) storage selection function framework. In the stationary special case, one can directly calculate the storage selection function from the age distribution of outflow alone (equation (8)), without any direct information concerning the age distribution of storage. This result establishes a quantitative framework for using stream water age distributions to estimate catchments' tendencies to release or retain waters of different ages.

Examples based on gamma distributions illustrate how streamflow ages translate into storage ages (Figure 3 and equations (10)–(13)). Our results show (Figure 3) that the mean age of stored water can range from half as old as streamflow (for plug flow conditions) to almost infinitely older (for strongly preferential flow). For

streamflow transit time distributions reported in the literature, we find that typical aquifers must be significantly older than the stream waters that drain them (Figure 4a), that they preferentially release the youngest stored waters to streamflow (Figures 4c and 4d), and that most streamflow originates from a thin veneer of total groundwater storage (Figure 4b).

This preferential release of young streamflow means that most groundwater is largely isolated from the surface, consistent with isotopic and geochemical tracer data suggesting that deep groundwaters are often very old [e.g., Jasechko et al., 2017]. Our method only quantifies storage ages in the thin veneer of groundwater that contributes disproportionately to the contemporary hydrologic cycle; the age distributions of deeper groundwaters that are largely isolated from the modern hydrologic cycle cannot be accurately constrained using stream water age data.

Where information is available for both storage ages and streamflow ages, our analysis establishes consistency relationships through which each could be used to better constrain the other. By quantifying the relationship between groundwater and streamflow ages, our analysis provides tools to jointly assess both of these important catchment properties.

Acknowledgments

The streamflow age distribution parameters used in this study are available in the cited references. We thank the Editor (M. Bayani Cardenas), Jana von Freyberg, Scott T. Allen, and two anonymous reviewers for their suggestions that helped to improve the manuscript.

References

- Ala-aho, P., C. Soulsby, H. Wang, and D. Tetzlaff (2017), Integrated surface-subsurface model to investigate the role of groundwater in headwater catchment runoff generation: A minimalist approach to parameterization, *J. Hydrol.*, *547*, 664–677.
- Ameli, A. A., J. J. McDonnell, and K. Bishop (2016), The exponential decline in saturated hydraulic conductivity with depth: A novel method for exploring its effect on water flow paths and transit time distribution, *Hydrol. Processes*, *30*, 2438–2450.
- Austin, A. T., L. Yahdjian, J. M. Stark, J. Belnap, A. Porporato, U. Norton, D. Ravetta, and S. M. Schaeffer (2004), Water pulses and biogeochemical cycles in arid and semiarid ecosystems, *Oecologia*, *141*, 221–235.
- Basu, N. B., et al. (2010), Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity, *Geophys. Res. Lett.*, *37*, L23404, doi:10.1029/2010GL045168.
- Benettin, P., C. Soulsby, C. Birkel, D. Tetzlaff, G. Botter, and A. Rinaldo (2017), Using SAS functions and high-resolution isotope data to unravel travel time distributions in headwater catchments, *Water Resour. Res.*, *53*, 1864–1878, doi:10.1002/2016WR020117.
- Berghuijs, W. R., M. Sivapalan, R. A. Woods, and H. H. G. Savenije (2014), Patterns of similarity of seasonal water balances: A window into streamflow variability over a range of time scales, *Water Resour. Res.*, *50*, 5638–5661, doi:10.1002/2014WR015692.
- Berkowitz, B. (2002), Characterizing flow and transport in fractured geological media: A review, *Adv. Water Resour.*, *25*, 861–884.
- Bethke, C. M., and T. M. Johnson (2008), Groundwater age and groundwater age dating, *Annu. Rev. Earth Planet. Sci.*, *36*, 121–152.
- Beven, K. (2006), A manifesto for the equifinality thesis, *J. Hydrol.*, *320*, 18–36.
- Beven, K., and P. Germann (1982), Macropores and water flow in soils, *Water Resour. Res.*, *18*, 1311–1325, doi:10.1029/WR018i005p01311.
- Beven, K., and P. Germann (2013), Macropores and water flow in soils revisited, *Water Resour. Res.*, *49*, 3071–3092, doi:10.1002/wrcr.20156.
- Bolin, B., and H. Rodhe (1973), A note on the concepts of age distribution and transit time in natural reservoirs, *Tellus*, *25*, 58–62.
- Botter, G. (2012), Catchment mixing processes and travel time distributions, *Water Resour. Res.*, *48*, W05545, doi:10.1029/2011WR011160.
- Botter, G., E. Bertuzzo, and A. Rinaldo (2011), Catchment residence and travel time distributions: The master equation, *Geophys. Res. Lett.*, *38*, L11403, doi:10.1029/2011GL047666.
- Cardenas, M. B. (2007), Potential contribution of topography-driven regional groundwater flow to fractal stream chemistry: Residence time distribution analysis of Tóth flow, *Geophys. Res. Lett.*, *34*, L05403, doi:10.1029/2006GL029126.
- Cardenas, M. B. (2008), Surface water-ground water interface geomorphology leads to scaling of residence times, *Geophys. Res. Lett.*, *35*, L08402, doi:10.1029/2008GL033753.
- Chesnaux, R., J. W. Molson, and R. P. Chapuis (2005), An analytical solution for ground water transit time through unconfined aquifers, *Ground Water*, *43*, 511–517.
- Cornaton, F., and P. Perrochet (2006a), Groundwater age, life expectancy and transit time distributions in advective–dispersive systems: 1. Generalized reservoir theory, *Adv. Water Resour.*, *29*, 1267–1291.
- Cornaton, F., and P. Perrochet (2006b), Groundwater age, life expectancy and transit time distributions in advective–dispersive systems: 2. Reservoir theory for sub-drainage basins, *Adv. Water Resour.*, *29*, 1292–1305.
- Crockford, R. H., and D. P. Richardson (2000), Partitioning of rainfall into throughfall, stemflow and interception: Effect of forest type, ground cover and climate, *Hydrol. Processes*, *14*, 2903–2920.
- Dai, A., and K. E. Trenberth (2002), Estimates of freshwater discharge from continents: Latitudinal and seasonal variations, *J. Hydrometeorol.*, *3*, 660–687.
- Dunn, S. M., C. Birkel, D. Tetzlaff, and C. Soulsby (2010), Transit time distributions of a conceptual model: Their characteristics and sensitivities, *Hydrol. Processes*, *24*, 1719–1729.
- Dunne, T. (1978), Field studies of hillslope flow processes, *Hillslope Hydrol.*, 227–293.
- Engdahl, N. B., and R. M. Maxwell (2015), Quantifying changes in age distributions and the hydrologic balance of a high-mountain watershed from climate induced variations in recharge, *J. Hydrol.*, *522*, 152–162.
- Eriksson, E. (1961), Natural reservoirs and their characteristics, *Geofis. Int.*, *1*, 27–43.
- Eriksson, E. (1971), Compartment models and reservoir theory, *Annu. Rev. Ecol. Syst.*, *2*, 67–84.
- Etcheverry, D., and P. Perrochet (2000), Direct simulation of groundwater transit-time distributions using the reservoir theory, *Hydrogeol. J.*, *8*, 200–208.
- Gibbs, R. J. (1970), Mechanisms controlling world water chemistry, *Science*, *170*, 1088–1090.
- Ginn, T. R. (1999), On the distribution of multicomponent mixtures over generalized exposure time in subsurface flow and reactive transport: Foundations, and formulations for groundwater age, chemical heterogeneity, and biodegradation, *Water Resour. Res.*, *35*, 1395–1407, doi:10.1029/1999WR900013.

- Gleeson, T., L. Smith, N. Moosdorf, J. Hartmann, H. H. Dürr, A. H. Manning, L. P. H. van Beek, and A. M. Jellinek (2011), Mapping permeability over the surface of the Earth, *Geophys. Res. Lett.*, **38**, L02401, doi:10.1029/2010GL045565.
- Gleeson, T., K. M. Befus, S. Jasechko, E. Luijendijk, and M. B. Cardenas (2016), The global volume and distribution of modern groundwater, *Nat. Geosci.*, **9**, 161–167.
- Godsey, S. E., et al. (2010), Generality of fractal 1/f scaling in catchment tracer time series, and its implications for catchment travel time distributions, *Hydrol. Processes*, **24**, 1660–1671.
- Goldsmith, G. R., L. E. Muñoz-Villiers, F. Holwerda, J. J. McDonnell, H. Asbjornsen, and T. E. Dawson (2012), Stable isotopes reveal linkages among ecohydrological processes in a seasonally dry tropical montane cloud forest, *Ecohydrology*, **5**, 779–790.
- Good, S. P., D. Noone, and G. Bowen (2015), Hydrologic connectivity constrains partitioning of global terrestrial water fluxes, *Science*, **349**, 175–177.
- Harman, C. J. (2015), Time-variable transit time distributions and transport: Theory and application to storage-dependent transport of chloride in a watershed, *Water Resour. Res.*, **51**, 1–30, doi:10.1002/2014WR015707.
- Heidbüchel, I., P. A. Troch, S. W. Lyon, and M. Weiler (2012), The master transit time distribution of variable flow systems, *Water Resour. Res.*, **48**, W06520, doi:10.1029/2011WR011293.
- Horton, R. E. (1933), The role of infiltration in the hydrologic cycle, *Eos Trans. AGU*, **14**, 446–460.
- Hrachowitz, M., C. Soulsby, D. Tetzlaff, I. A. Malcolm, and G. Schoups (2010), Gamma distribution models for transit time estimation in catchments: Physical interpretation of parameters and implications for time-variant transit time assessment, *Water Resour. Res.*, **46**, W10536, doi:10.1029/2010WR009148.
- Hrachowitz, M., P. Benettin, B. M. Van Breukelen, O. Fovet, N. J. Howden, L. Ruiz, Y. van der Velde, and A. J. Wade (2016), Transit times—The link between hydrology and water quality at the catchment scale, *Wiley Interdiscip. Rev. Water*, **3**, 629–657.
- Jasechko, S., J. W. Kirchner, J. M. Welker, and J. J. McDonnell (2016), Substantial proportion of global streamflow less than three months old, *Nat. Geosci.*, **9**, 126–129.
- Jasechko, S., et al. (2017), Global aquifers dominated by fossil groundwaters but wells vulnerable to modern contamination, *Nat. Geosci.*, **10**, 425–429, doi:10.1038/ngeo2943.
- Kazemi, G. A., J. H. Lehr, and P. Perrochet (2006), *Modeling of Groundwater Age and Residence Time Distributions*, in *Groundwater Age*, John Wiley, Hoboken, N. J.
- Kim, M., L. A. Pangle, C. Cardoso, M. Lora, T. H. M. Volkmann, Y. Wang, C. J. Harman, and P. A. Troch (2016), Transit time distributions and StorAge Selection functions in a sloping soil lysimeter with time-varying flow paths: Direct observation of internal and external transport variability, *Water Resour. Res.*, **52**, 7105–7129, doi:10.1002/2016WR018620.
- Kirchner, J. W. (2003), A double paradox in catchment hydrology and geochemistry, *Hydrol. Processes*, **17**, 871–874.
- Kirchner, J. W. (2016), Aggregation in environmental systems—Part 2: Catchment mean transit times and young water fractions under hydrologic nonstationarity, *Hydrol. Earth Syst. Sci.*, **20**, 299–328.
- Kirchner, J. W., X. Feng, and C. Neal (2000), Fractal stream chemistry and its implications for contaminant transport in catchments, *Nature*, **403**, 524–527.
- Kirchner, J. W., X. Feng, and C. Neal (2001), Catchment-scale advection and dispersion as a mechanism for fractal scaling in stream tracer concentrations, *J. Hydrol.*, **254**, 81–100.
- Kollet, S. J., and R. M. Maxwell (2008), Demonstrating fractal scaling of baseflow residence time distributions using a fully-coupled groundwater and land surface model, *Geophys. Res. Lett.*, **35**, L07402, doi:10.1029/2008GL033215.
- Leray, S., N. B. Engdahl, A. Massoudieh, E. Bresciani, and J. Mccallum (2016), Residence time distributions for hydrologic systems: Mechanistic foundations and steady-state analytical solutions, *J. Hydrol.*, **543**, 67–87.
- Maxwell, R. M., L. E. Condon, S. J. Kollet, K. Maher, R. Haggerty, and M. M. Forrester (2016), The imprint of climate and geology on the residence times of groundwater, *Geophys. Res. Lett.*, **43**, 701–708, doi:10.1002/2015GL066916.
- McDonnell, J. J., and K. Beven (2014), Debates—The future of hydrological sciences: A (common) path forward? A call to action aimed at understanding velocities, celerities and residence time distributions of the headwater hydrograph, *Water Resour. Res.*, **50**, 5342–5350, doi:10.1002/2013WR015141.
- McDonnell, J. J., et al. (2007), Moving beyond heterogeneity and process complexity: A new vision for watershed hydrology, *Water Resour. Res.*, **43**, W07301, doi:10.1029/2006WR005467.
- McGuire, K. J., and J. J. McDonnell (2006), A review and evaluation of catchment transit time modeling, *J. Hydrol.*, **330**, 543–563.
- Rinaldo, A., K. J. Beven, E. Bertuzzo, L. Nicotina, J. Davies, A. Fiori, D. Russo, and G. Botter (2011), Catchment travel time distributions and water flow in soils, *Water Resour. Res.*, **47**, W07537, doi:10.1029/2011WR010478.
- Rinaldo, A., P. Benettin, C. J. Harman, M. Hrachowitz, K. J. McGuire, Y. van der Velde, E. Bertuzzo, and G. Botter (2015), Storage selection functions: A coherent framework for quantifying how catchments store and release water and solutes, *Water Resour. Res.*, **51**, 4840–4847, doi:10.1002/2015WR017273.
- Rodell, M., et al. (2015), The observed state of the water cycle in the early twenty-first century, *J. Clim.*, **28**, 8289–8318.
- Seeger, S. (2013), Transit times and storage properties of mesoscale catchments in Switzerland, MS thesis, 80 pp., Univ. of Freiburg, Freiburg.
- Seeger, S., and M. Weiler (2014), Reevaluation of transit time distributions, mean transit times and their relation to catchment topography, *Hydrol. Earth Syst. Sci.*, **18**, 4751–4771.
- Sklash, M. G., and R. N. Farvolden (1979), The role of groundwater in storm runoff, *J. Hydrol.*, **43**, 45–65.
- Soulsby, C., C. Birkel, and D. Tetzlaff (2016), Characterizing the age distribution of catchment evaporative losses, *Hydrol. Processes*, **30**, 1308–1312.
- Stark, C. P., and M. Stieglitz (2000), Hydrology: The sting in a fractal tail, *Nature*, **403**, 493–495.
- Stewart, M. K., and J. J. McDonnell (1991), Modeling base flow soil water residence times from deuterium concentrations, *Water Resour. Res.*, **27**, 2681–2693, doi:10.1029/91WR01569.
- Tetzlaff, D., C. Soulsby, M. Hrachowitz, and M. Speed (2011), Relative influence of upland and lowland headwaters on the isotope hydrology and transit times of larger catchments, *J. Hydrol.*, **400**, 438–447.
- Toews, M. W., C. J. Daughney, F. J. Cornaton, U. Morgenstern, R. D. Evison, B. M. Jackson, K. Petrus, and D. Mzila (2016), Numerical simulation of transient groundwater age distributions assisting land and water management in the Middle Wairarapa Valley, New Zealand, *Water Resour. Res.*, **52**, 9430–9451, doi:10.1002/2016WR019422.
- Torgersen, T., R. Purtschert, F. M. Phillips, L. N. Plummer, W. E. Sanford, and A. Suckow (2013), *Defining Groundwater Age. Isotope Methods for Dating Old Groundwater*, International Atomic Energy Agency, Vienna, Austria.

- Turner, J. V., and C. J. Barnes (1998), *Isotope Tracers in Catchment Hydrology*, edited by C. Kendall and J. J. McDonnell, pp. 723–760, Elsevier, Amsterdam.
- van der Velde, Y., P. J. J. F. Torfs, S. E. A. T. M. van der Zee, and R. Uijlenhoet (2012), Quantifying catchment-scale mixing and its effect on time-varying travel time distributions, *Water Resour. Res.*, *48*, W06536, doi:10.1029/2011WR011310.
- Weiler, M., B. L. McGlynn, K. J. McGuire, and J. J. McDonnell (2003), How does rainfall become runoff? A combined tracer and runoff transfer function approach, *Water Resour. Res.*, *39*(11), 1315, doi:10.1029/2003WR002331.
- Wörman, A., A. I. Packman, L. Marklund, J. W. Harvey, and S. H. Stone (2007), Fractal topography and subsurface water flows from fluvial bedforms to the continental shield, *Geophys. Res. Lett.*, *34*, L07402, doi:10.1029/2007GL029426.